

REFERENCE NO.

35

In re application of: Gang Sun, et al.
Application No.: 10/674,764
Filing Date: September 29, 2003
Attorney Docket No.: 18062G-002910US

PATENT SPECIFICATION

(11) 1 474 482

1 474 482

- (21) Application No. 36192/74 (22) Filed 16 Aug. 1974
 (31) Convention Application No. 2341426 (32) Filed 16 Aug. 1973 in
 (33) Federal Republic of Germany (DT)
 (44) Complete Specification published 25 May 1977
 (51) INT CL² D06P 1/08 3/52 3/76
 (52) Index at acceptance
 D1B 2L16 2L1B 2L29A 2L2A 2L3 2L5D2 2L5D 2L7 2L9



(54) PROCESS FOR DYEING FIBRE MATERIALS WHICH CAN BE DYED WITH CATIONIC DYES

(71) We, HOECHST AKTIENGESSELLSCHAFT, a body corporate organised according to the laws of the Federal Republic of Germany, of 6230 Frankfurt/Main 80, Federal Republic of Germany, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

It is known that acidic or acidically modified fibres, such as polyacrylonitrile fibres or anionically modified polyester fibres, can be dyed continuously with cationic dyestuffs using aqueous padding baths and a subsequent fixation of the dyestuffs at an elevated temperature. According to this method, a suitable cationic dyestuff in an aqueous solution is padded onto the fabric, the dyeing is, if desired, subjected to an intermediate drying, and is then fixed for some minutes at 100° to 103°C, preferably in the presence of steam. This process is followed by a rinsing process. These dyeings have very good fastness properties and are distinguished especially by a very good fastness to thermofixation.

Furthermore it is known from US Patent Specification No. 2,663,612 that synthetic fibres in the form of plane articles can be dyed with water-insoluble disperse dyestuffs according to the Thermosol process. This process involves the following steps: padding of the dyestuff dispersion, drying, fixation by dry heat at a temperature between 200°C and 230°C, and a subsequent reductive after-treatment, during which the portion of the disperse dyestuffs which has not been fixed, i.e. that does not penetrate into the fibre, is removed and destroyed. This process is followed by rinsing. The dyeings thus prepared do not depend very much on the fibre material (polyacrylonitrile, polyamide, polyester fibres) with regard to their fastness to sublimation, to dry heat fixation, to pleating or to thermofixation, but depend especially on the character of the dyestuff, on its constitution and on the application process.

When polyacrylonitrile fibres are used, only low temperatures can be used in the Thermosol process, on account of the thermal properties of this fibre (softening range: 190° to 20°C). The application of disperse dyestuffs having a high fastness to sublimation is not reasonable in the case of such low temperatures, due to the reduced color build-up capacity; therefore, such processes have not obtained any importance in practice. Furthermore, the other fastness properties of these dyeings with disperse dyestuffs are not satisfactory.

The present invention provides a continuous process for dyeing a textile material comprising acidic synthetic fibres which can be dyed with cationic dyes, for example polyacrylonitrile or anionically modified polyester fibres, which comprises impregnating, preferably by padding, the material with an aqueous solution containing a water-insoluble azo dyestuff having a molecular weight in the range of from 200 to 500, preferably from 250 to 350, a vapour pressure of more than 20 microbars at 160°C, and at least one substituted or unsubstituted amino group capable of forming a salt with an acid, which dyestuff has been made water-soluble by reaction with an acid which becomes volatile at a temperature of about 100°C, drying the textile material, thermosoling the material at a temperature below the softening point of the corresponding fibre substance, and subsequently treating the textile material with a hot, dilute, strongly dissociated, volatile or non-volatile acid.

The dyeing may then be completed in the usual manner.

The process of the invention can be carried out in a simple manner and without any special equipment. It allows the use of dyestuffs without finish treatment, and some dyestuffs which normally have not been considered hitherto for textile purposes.

To be suitable for the process of the invention the dyestuffs must have the following properties:

- (i) azo groups as chromophores;
- (ii) at least one (substituted or unsubstituted) amino group capable of forming a salt with an acid; that means a dyestuff base;
- (iii) a distinct vapour pressure at the thermosoling temperature i.e. more than 20 microbars at 160°C, and a molecular weight of from 200 to 500, preferably 250 to 350;
- (iv) as the free dyestuff base-being difficultly soluble or insoluble in water, but as a salt of a volatile acid—being readily soluble in water at room temperature.

The dyestuff bases of this type are converted into their water-soluble salts with acids which are volatile at drying temperatures, i.e. approximately 100°C, and aqueous solutions of these salts are padded onto acidic fibres, such as polyacrylonitrile or anionically modified polyester fibres, and dried at elevated temperatures of 100° to 110°C. During the drying a splitting to the volatile acid and to the free dyestuff base occurs, whereby the latter remains on the fibre surface. Subsequently the thermosol process is carried out. In the case of polyacrylonitrile fibres the thermosoling temperature is generally in the range of from 150° to 170°C, preferably about 160°C, and in the case of acidically modified polyester fibres it is generally in the range of from 190° to 210°C, preferably about 200°C. The duration of the thermosol operation generally is from 30 to 90 seconds, preferably 60 seconds.

By the action of heat the molecule of the dyestuff base is strongly activated, which brings about sublimation. The limited size of the molecule of the base in the vapour phase permits the simultaneous diffusion into the fibre.

After the thermosol process the dyed material is treated continuously, for example in several boxes of a full-width washing device, preferably at boiling temperature, with one or more diluted strong acids, preferably mineral acids. During this treatment not only is unfixed dyestuff base removed from the fibre surface, but also the dyestuff base which is in the fibre is reconverted into a salt. This salt, consisting of dyestuff base and acid, has a considerably lower vapour pressure than the free dyestuff base within the fibre (probably because of its salt-forming component); however, the vapour pressure of the colouring substance is reduced by up to two powers of ten, so that dyeings having a good fastness to thermofixation are obtained. The process is usually concluded by the normal rinsing processes and by drying.

Generally one mol of a volatile acid per mol of dyestuff base is required in order to form the soluble salt. In the case of dyestuff bases having more than one amino group capable of forming salts, one mole of acid is also sufficient to ensure a sufficient solubility in padding liquor concentrations. The stoichiometrical proportions can be somewhat rounded off in favour of the acid, in order to accelerate the dissolution of the dyestuff base. However, large excesses of acid or the use of non-volatile acids for the formation of the water-soluble dyestuff salt must be avoided for a better dyestuff yield.

Whereas for the dissolution of the dyestuff base in the preparation of the padding liquors only volatile acids are suitable, it is possible, and even recommendable, for the acidic treatment after thermofixation to use non-volatile acids (for example sulphuric acid), since in this case only the strength of the acid (very low pH-value) is important. This after-treatment is expediently carried out at acid concentrations of 0.1 to 1.0 mol per litre.

Suitable volatile acids are, for example:

Hydrochloric acid

1 Litre of commercial hydrochloric acid of 20° Bé (=32.1% by weight) contains 373 g of HCl or 11.25 mols of HCl,
97.8 ml of HCl contain 1 mol (36.46 g of HCl)

Acetic acid

1 Litre of commercial 60% acetic acid (by weight) contains 641.1 g of CH₃COOH or 10.7 mols of CH₃COOH,
93.6 ml of CH₃COOH contain 1 mol (60 g of CH₃COOH)
1 Litre of commercial 80% acetic acid (by weight) contains 860 g of CH₃COOH of 14.3 mols of CH₃COOH,
69.8 ml of CH₃COOH contain 1 mol (60 g of CH₃COOH)

1 Litre of 100% acetic acid (by weight—glacial acetic acid) contains 1050 g of CH_3COOH or 17.6 mols,
57.8 ml contain 1 mol (60 g of CH_3COOH)

Formic acid

1 Litre of commercial 85% formic acid (by weight) contains 1016 g of HCOOH
or 22.2 mols of HCOOH
46 ml of HCOOH contains 1 mol (46 g of HCOOH).

In most cases the colour of the solution of the dyestuff base as the hydrochloride, acetate or formate is different from the colour of the free dyestuff base.

Since the necessary treatment with a hot solution of a diluted strong acid causes the desired thermostable salt of the dyestuff base and acid to be reprepared (with participation of the acidic fibre), the dyeing of the textile material has a shade which corresponds to that of the solution and not to that of the free dyestuff base. If this acidic treatment is not applied, the fastness to dry heat of the dyeing is considerably lower and the sublimation on the thermostest device begins at a temperature up to 40°C lower than in the case of the dyeing regularly treated with acid.

Aminoazo dyestuffs which may be used for the process according to the invention are known, and are described, for example, in the Colour Index.

The following Examples illustrate the invention.

EXAMPLE 1:

A fabric of polyacrylonitrile fibres was padded at room temperature, with a liquor pick-up of 80% (calculated on the weight of the dry material), with an aqueous bath which contained, per litre, 40 g of 2,4-diamino-azobenzene-monohydrochloride, formed from 34.2 g of 2,4-diamino-azobenzene and 16.5 ml of hydrochloric acid of 20° Bé (=32.1% by weight).

Then the padded material was dried for about 60 seconds at 100°C, and the dyestuff applied was thermofixed in the form of the free base for 60 seconds at 160°C with dry heat. The textile material was subsequently treated for 5 minutes with an aqueous bath, at boiling temperature, which contained 10 ml/l of hydrochloric acid of 20° Bé.

The dyeing was rinsed with warm and cold water as usual and dried. A brilliant golden yellow dyeing having an excellent fastness to thermofixation was obtained.

If, in the above dyeing, the acidic treatment of the material dyed with the dyestuff base was not carried out, the sublimation of the dyestuff on the thermostest device began at a temperature which was 40°C lower than in the case of the dyeing treated with acid.

EXAMPLE 2:

The dyeing was carried out as described in Example 1, but using a fabric of anionically modified polyester fibres. The padded material was thermofixed at 200°C for 60 seconds. An intense golden-yellow dyeing having a very good fastness to thermofixation was obtained.

EXAMPLE 3:

A fabric of polyacrylonitrile fibres was padded on a foulard at room temperature, with a liquor pick-up of 80% by weight, with an aqueous bath which contained per litre 25 g of 4-dimethylamino-azobenzene, dissolved in 10.5 ml of acetic acid (60%).

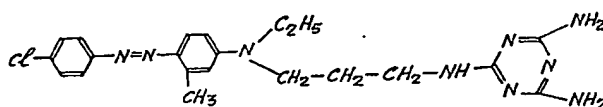
The textile material was dried for 60 seconds at 100°C, and then thermoset for 60 seconds at 160°C to fix the colour base.

Subsequently the material thus treated was led directly and continuously through a boiling aqueous bath containing 3 ml/l of 96% sulphuric acid (by weight) in several boxes of a full-width washing device, the residence time being 3 to 5 minutes. The dyeing was rinsed with warm and cold water and dried. A red dyeing having a very good fastness to thermofixation was obtained.

For dyeings according to Examples 1 to 3 the following dyestuff bases having the properties required are suitable:

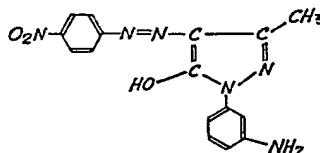
EXAMPLE 4:

Shade on PAC: brilliant pink; molecular weight 427.5. Acid required for dissolution of 100 g of pure dyestuff: 0.234 mol.

**EXAMPLE 5:**

Shade on PAC: golden yellow; molecular weight 340. Acid required for dissolution of 100 g of pure dyestuff: 0.295 mol.

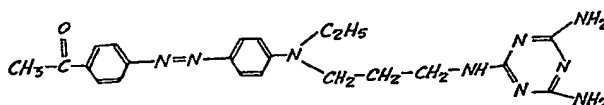
5



5

EXAMPLE 6:

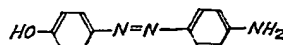
Shade on PAC: pink; molecular weight 391. Acid required for dissolution of 100 g of pure dyestuff: 0.256 mol.



10

EXAMPLE 7:

Shade on PAC: bluish red; molecular weight 213. Acid required for dissolution of 100 g of pure dyestuff: 0.472 mol.

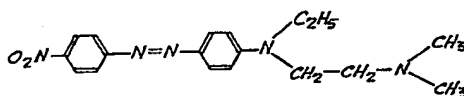


10

EXAMPLE 8:

Shade on PAC: red; molecular weight 375.5. Acid required for dissolution of 100 g of pure dyestuff: 0.267 mol.

15



15

EXAMPLE 9:

Shade on PAC: pink; molecular weight 278. Acid required for dissolution of 100 g of pure dyestuff: 0.360 mol.

20

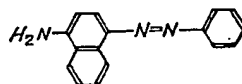


20

EXAMPLE 10:

Shade on PAC: violet; molecular weight 247. Acid required for dissolving 100 g of pure dyestuff: 0.405 mol.

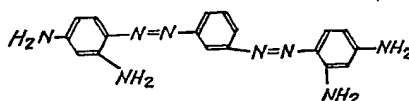
25



25

EXAMPLE 11:

Shade on PAC: brown; molecular weight 338. Acid required for dissolving 100 g of pure dyestuff: 0.296 mol.



WHAT WE CLAIM IS:—

1. A continuous process for dyeing a textile material comprising acidic synthetic fibres which can be dyed with cationic dyes, which comprises impregnating the material with an aqueous solution containing a water-insoluble azo dyestuff having a molecular weight in the range of from 200 to 500, a vapour pressure of more than 20 microbars at 160°C, and at least one substituted or unsubstituted amino group capable of forming a salt with an acid, which dyestuff has been made water-soluble by reaction with an acid volatile at a temperature of approximately 100°C, drying the textile material, thermosoling the material at a temperature below the softening point of the corresponding fibre substances, and subsequently treating the textile material with a hot, dilute, strongly dissociated, volatile or non-volatile acid.
2. A process as claimed in claim 1, wherein the impregnation of the textile material with the aqueous dyestuff solution is carried out according to a padding method.
3. A process as claimed in claim 1 or claim 2, wherein the water-insoluble azo dyestuff has a molecular weight in the range of from 250 to 350.
4. A process as claimed in any one of claims 1 to 3, wherein the drying operation is carried out at a temperature of from 100°C to 110°C.
5. A process as claimed in any one of claims 1 to 4, wherein the volatile acid used to render the dyestuff water soluble is hydrochloric acid, acetic acid or formic acid.
6. A process as claimed in any one of claims 1 to 5, wherein the textile material comprises polyacrylonitrile fibres and the thermosoling is carried out at a temperature in the range of from 150° to 170°C.
7. A process as claimed in claim 6, wherein the thermosoling temperature is 160°C.
8. A process as claimed in any one of claims 1 to 5, wherein the textile material comprises acidically modified polyester fibres and the thermosoling is carried out at a temperature in the range of from 190° to 210°C.
9. A process as claimed in claim 8, wherein the thermosoling temperature is 200°C.
10. A process as claimed in any one of claims 1 to 9, wherein the thermosoling operation is carried out within a period of from 30 to 90 seconds.
11. A process as claimed in claim 10, wherein the thermosoling period is 60 seconds.
12. A process as claimed in any one of claims 1 to 11, wherein the acid used in the acid after-treatment is a mineral acid.
13. A process as claimed in any one of claims 1 to 12, wherein the acid after-treatment is carried out at boiling temperature and at an acid concentration of from 0.1 to 1.0 mol per litre.
14. A process as claimed in claim 1, conducted substantially as described herein.
15. A process as claimed in claim 1, conducted substantially as described in any one of the Examples.
16. A textile material comprising acidic synthetic fibres which can be dyed with cationic dyes, whenever dyed by a process as claimed in any one of claims 1 to 15.
17. A textile material comprising polyacrylonitrile or acidically modified polyester fibres, whenever dyed by a process as claimed in any one of claims 1 to 15.

ABEL & IMRAY,
Chartered Patent Agents,
Northumberland House,
303—306 High Holborn,
London, WC1V 7LH.